Universidad de Huelva

Radiation Physics and Environment Group

VALORIZATION OF WASTE COMING FROM TITANIUM DIOXIDE AND PHOSPHATE FERTILIZER NORM INDUSTRIES IN SULFUR POLYMER CONCRETE

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INTRODUCTION

✓ **The valorisation of NORM waste adds a new aspect: the associated radiological problem.**

✓ **The present study has been carried out with the aim of evaluating the radiological problem related to the valorization of two wastes from the TiO_2 and phosphoric acid NORM industries.**

✓ **The factory of Tioxide-Huelva (TiO2) is the only one in Spain devoted to the titanium dioxide production.**

✓ **Two residues has been studied: 1) Phosphogypsum from phosphoric acid industry, and 2) un-attacked mud from the mineral digestion.**

LOCATION

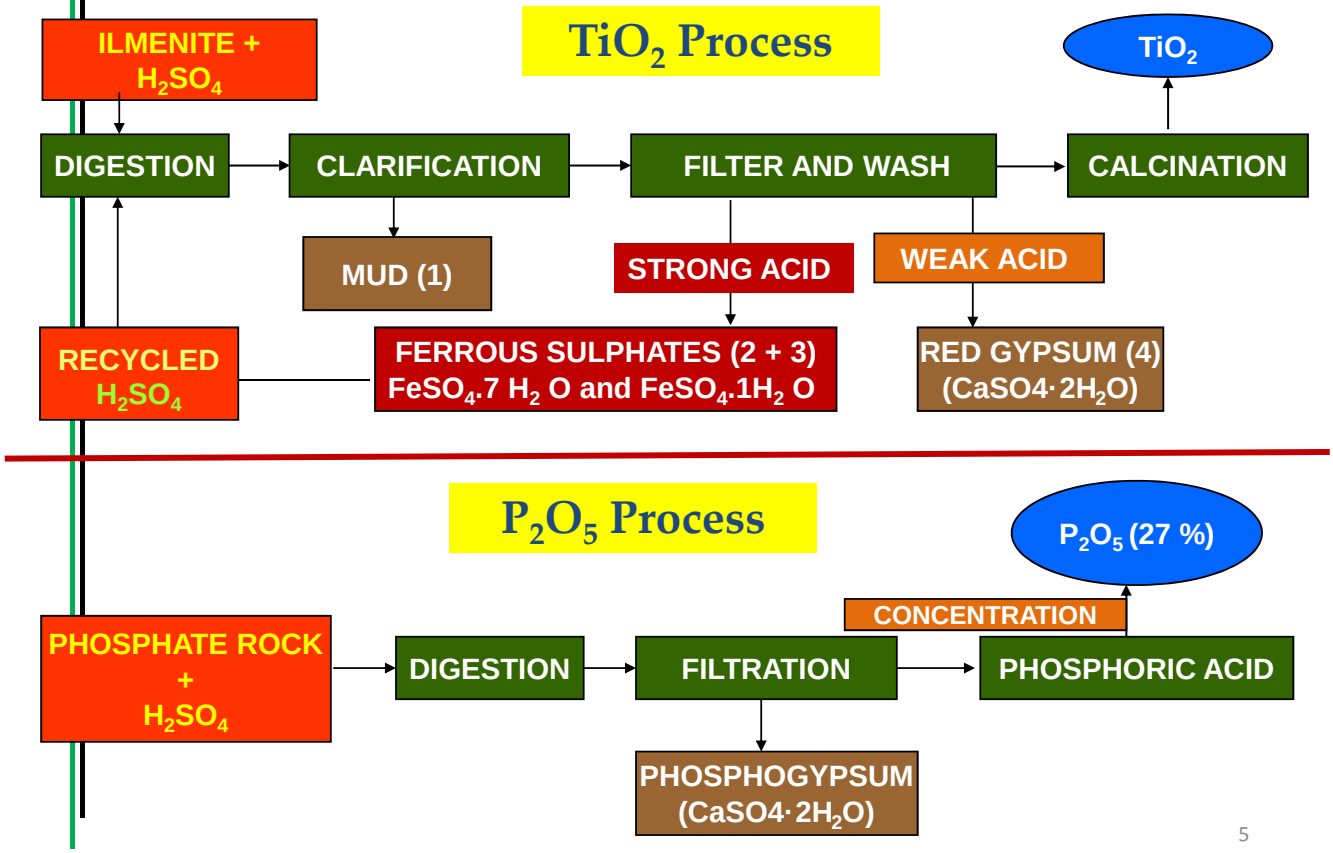
OBJETIVES

✓ To characterize two waste (PG and MUD), in elemental composition, mineralogy, granulometry and radioactive contents.

✓ To check the possibility to use these waste as additive in sulfur polymer cements (SPC): fast setting times (< 1 day), high durability, rapid gain of high strength, to isolate dangerous wastes, etc.

✓ To evaluate the degree of stabilization/ solidification of both phosphogypsum (PG) and mud (MD) inside the matrix cement taking in to account the leaching test.

INDUSTRIAL PROCESS



MATERIALS

✓ MUD and PG samples were collected every 5 days for 1 month, in order to evaluate the possible temporal variability of the characteristics of these materials.

✓ A granular elemental sulfur (supplied by Repsol Madrid, Spain), gravel and a siliceous sand were used.

✓ A modified sulfur containing polymer (STX™) was used as thermoplastic material.

CHARACTERISATION OF PHOSPHOGYPSUM AND MUD

MAJOR ELEMENTS

Table 1. Concentration (%) of major elements in the components of SPC cements

	LOI	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	TiO_2	SO_3	P_2O_5	K_2O	Na_2O
PG	2.4	2.43	0.4	40.3	0.23	0.04	0.04	52.41	0.95	0.03	0.13
MUD	11.19	11.88	1.44	0.73	12.49	0.94	52.92	7.79	0.02	0.16	0.16
Gravel	7.86	29.12	1.27	57.83	0.8	0.63	0.13	0.27	-----	0.25	-----
Sand	8.9	79.89	10.75	0.42	0.74	0.26	0.11	-----	-----	5.3	1.78

- The main components in PG are Ca (as CaO 40%) and S (as SO_3 with 54 %) with impurities of Si (2.5%) and P_2O_5 (1%) .
- Mud sample shows a high concentration of TiO_2 (53 %) and significant concentrations of Fe and Si oxides around 12 % → possible applications for its high content in TiO_2.

GRANULOMETRY

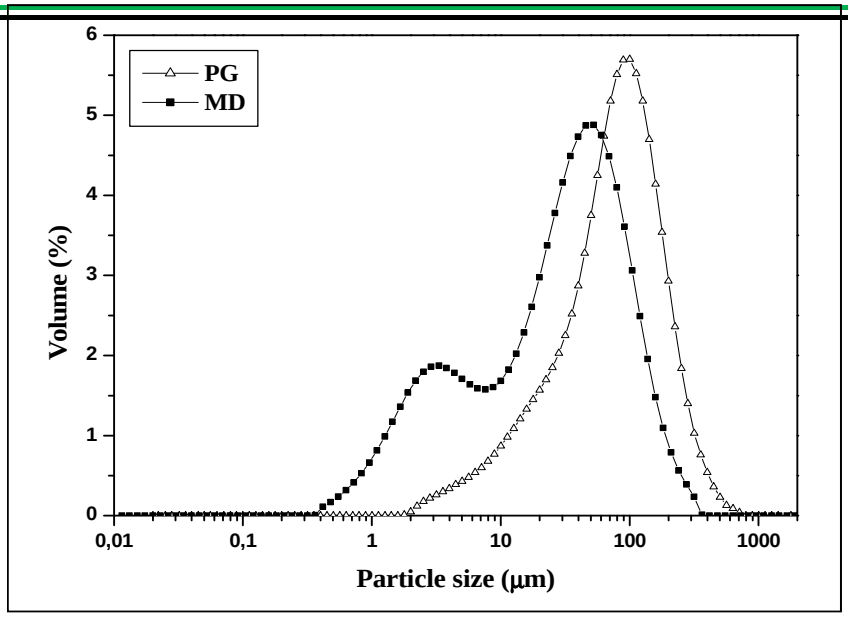
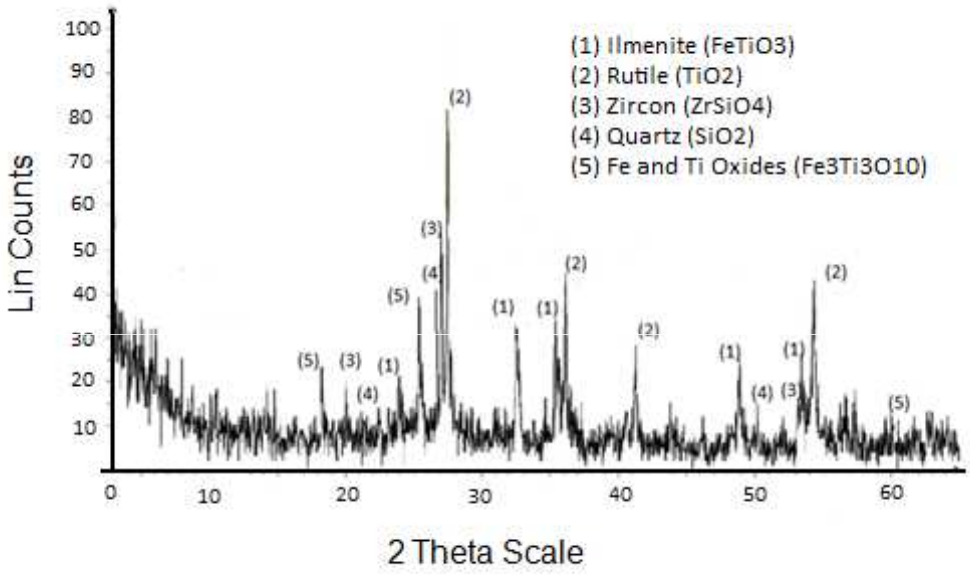


Figure 1. The particle size distribution of waste samples (PG and MD)

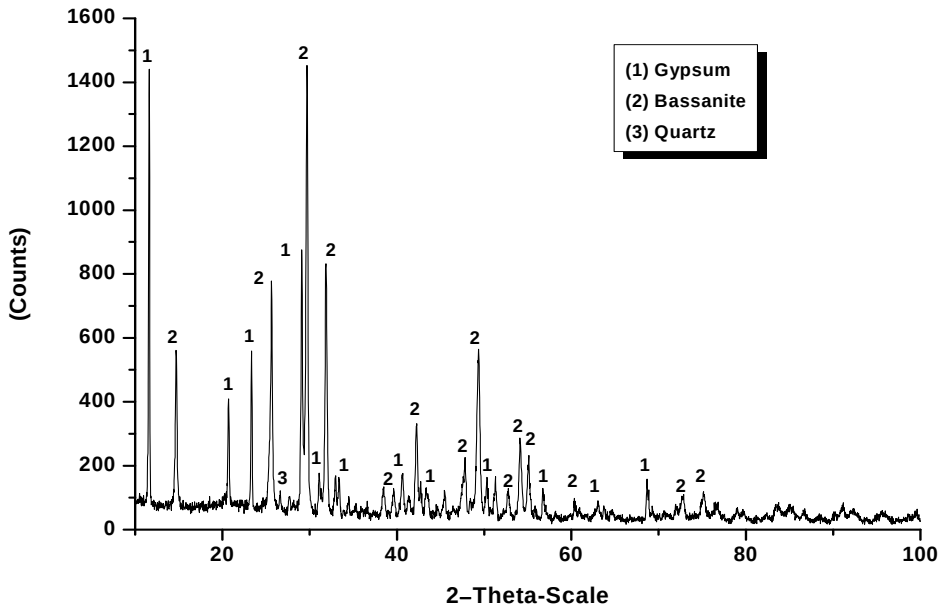
- **The median value of particle diameter in phosphogypsum and mud were about 53 µm and 30 µm, respectively.**
- **The particle size of the mud is smaller than in the phosphogypsum.**

XRD (Mud)



Mud (Figure left) shows several mineralogical species : ilmenite, rutile, zircon ($ZrSiO_4$), quartz (SiO_2), and Fe and Ti oxides ($Fe_3Ti_3O_{10}$).

XRD (Phosphogysum)



PG (Figure right) contains two main crystalline phases of $CaSO_4 \cdot 2H_2O$: a) gypsum, b) bassanite. And some impurities of quartz.

ACTIVITY CONCENTRATION

Table 2. Activity concentration (Bq/kg) of MUD and PG samples.

Code	PHOSPHATE ROCK	PG	ILMENITE	MD
^{210}Pb	1600 ± 90	624±37	82 ± 4	247 ± 11
^{238}U	1650 ± 70	97±6	105 ± 10	184 ± 12
^{232}Th	25 ± 2	8.2±1.0	315 ± 20	250 ± 15
^{226}Ra	1580 ± 80	589±34	110 ± 10	521 ± 30
^{228}Ra	22 ± 2	8±1	300 ± 20	1919 ± 112
^{40}K	< 18	< 18	30 ± 5	334 ± 21

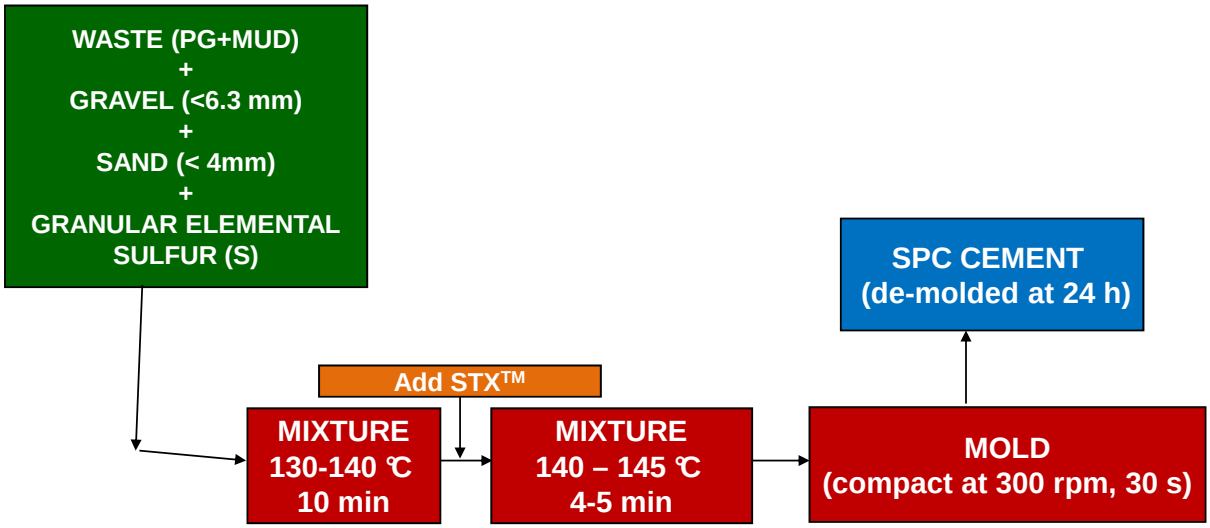
TITANIUM DIOXIDE: 1 g of Raw Material → 0.10 g MUD (dry); 0.48 g Pigment

PHOSPHORIC ACID: 1 g of Raw Material → 1 g Phosphoric acid (27% P2O5); 1.5 g PG

VALORISATION OF PHOSPHOGYPSUM AND MUD

- Currently, the MUD generated is stored in an authorized industrial dangerous repository, while PG is in big stacks very close the P2O5 plants.
- We have analyzed the possibility of use PG and MUD as **additive in sulfur polymer cements** (SPC).
- **6 mixtures** were studied, codified as **SPC-X-Y-Z** where "X" is the king of waste incorporated, "Y" is the wt % of elemental sulfur, and "Z" is the percentage wt% of the waste in the mixtures (Example: SPC-MD-21-20).
- The properties of them **were compared** with a commercial cement **CEM** (type I 52.5 N/SR) and SPC-21, which were taken as **reference cement**.

PRODUCTION PROCESS OF SPC CEMENTS



SAMPLES PREPARATION

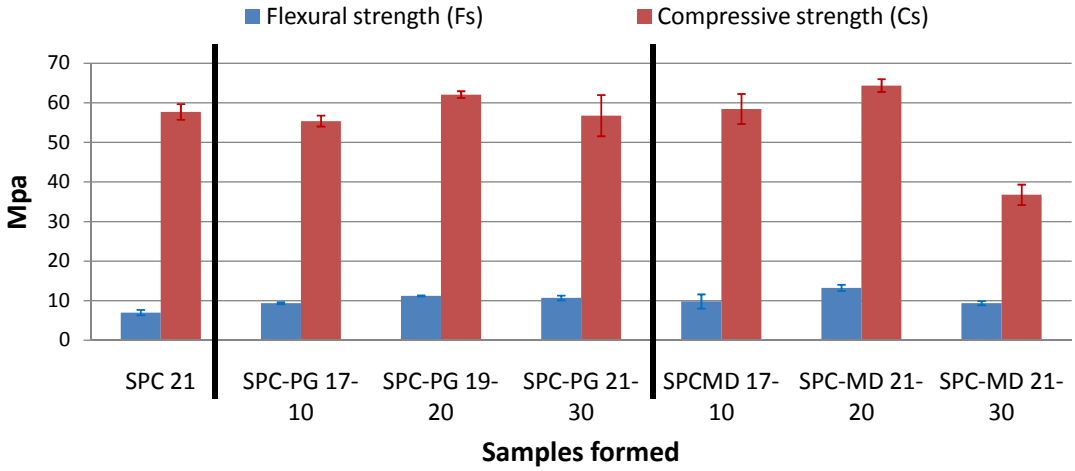
Table 3. Composition of different sulfur polymer cement samples with phosphogypsum (PG) (SPC-PG) and with mud (SPC-MD) (expressed as wt %). SPC-21 has taken as reference.

Samples	Elemental Sulfur (S)	Gravel	Sand	PG	MD	Modified sulfur (STX™)	Ratio Elem. S/waste
SPC-21*	21.00	23.10	46.14	10% (CaCO3)		2.10	0.70
SPC-PG-17-10	17.00	23.77	47.53	10.00		1.70	1.70
SPC-PG-19-20	19.00	19.70	39.40	20.00		1.90	0.95
SPC-PG-21-30	21.00	15.63	31.27	30.00		2.10	0.70
SPC-MD-17-10	17.00	23.77	47.53		10.00	1.70	1.70
SPC-MD-21-20	21.00	18.97	37.93		20.00	2.10	1.05
SPC-MD-21-30	21.00	15.63	31.27		30.00	2.10	0.70

*) **SPC-21** contains 10% calcium carbonate as inert substituting the waste

Ratio Gravel/Sand= 0.50; ratio Sulfur/STX™= 10.00

MECHANICAL TEST



- The Cs of the SPCs has values between 55 and 62 MPa for PG, and 36 to 64 MPa for MD cements, similar o even better than SPC taken as reference.
- A Portland Commercial cement present a Fs = 10.1 ± 1.2 MPa for 28 days of age, and Cs = 61.3 ± 1.0 MPa for 28 days.

ACTIVITY CONCENTRATION

Table 4. Activity concentration (Bq/kg) in different samples.

Code	SPC-21	SPC-PG 17-10	SPC-PG 19-20	SPC-PG 21-30	SPC-MD 17-10	SPC-MD 21-20	SPC-MD 21-30
% Waste	0	10	20	30	10	20	30
^{210}Pb	8.0 ± 0.6	70±5	143±9	219±13	28 ± 4	40 ± 4	76 ± 7
^{238}U	12±2	21±2	12±2	38±3	25 ± 4	61 ± 5	84 ± 7
^{232}Th	9.1±0.7	9.4±0.7	8.6±0.6	8.1±0.5	54 ± 3	115 ± 7	182 ± 11
^{226}Ra	**7.4 ± 0.5**	**63±4**	**115±7**	**179±11**	51 ± 3	123 ± 7	194 ± 11
^{228}Ra	8.2±0.8	8.6±0.8	8.8±0.8	6.9±0.7	**212 ± 13**	**426 ± 26**	**674 ± 39**
^{40}K	**580±30**	**528±32**	**394±24**	**347±21**	512 ± 31	493 ± 32	413 ± 24

- Activity concentration of ^{226}Ra shows a linear dependence (**$y = 5.49 \cdot x + 8.95$; $R^2 = 0.9988$**) with the percentage (x) of **PG** added.
- ^{40}K concentration decreases linearly: **$y = -5.82 \cdot x + 529$; $R^2 = 0.9041$**

- ^{228}Ra shows a linear dependence (**$y = 18.7 \cdot x + 59.6$; $R^2 = 0.9976$**) with the percentage of **MUD** added. Similar behavior we see for the ^{210}Pb, ^{234}Th and ^{232}Th.

RADIOLOGICAL EVALUATION

$$I = \frac{C226_{Ra}}{300 Bqkg^{-1}} + \frac{C228_{Ra}}{200 Bqkg^{-1}} + \frac{C40_{k}}{3000 Bqkg^{-1}}$$

$$Ra(eq) = C_{226Ra} + 1.43 C_{228Ra} + 0.077 C_{40K}$$

Code	SPC-21	SPC-PG 17-10	SPC-PG 19-20	SPC-PG 21-30	SPC-MD 17-10	SPC-MD 21-20	SPC-MD 21-30
% Waste	0	10	20	30	10	20	30
Index "I"	**0.26**	**0.43**	**0.56**	**0.75**	**1.4**	**2.7**	**4.2**
Ra (eq)	64	117	158	216	394	770	1189

- In **SPC-PG** samples, Index I are below the EU reference value (**I<1**) for **bulk building materials**. I < 6 for thin elements (< 2 mm in thickness).

- In SPC-MD, index *I* is higher than EU reference value in bulk materials, but lesser than for superficial and other materials with restricted use (I<6).

ACELERATED LEACHING TESTS

- The leaching experiments of SPC samples were tested as follow: Firstly, were immersed in demineralised water for 24 h, and secondly they were dried, weighed, and again submerged for 42 days in 250 mL of buffer solutions at different pH (2-10) (n = 3 for each pH). The **coefficient of absorption** respect to the pH, A_C, were calculated.

$$A_c\ (\%) = \frac{P_{3i} - P_{1i}}{P_{1i}} \cdot 100$$

- After the 42-day the solutions were filtered and their radionuclide concentrations determined. The percentage of each leached radionuclide was determined by the **leaching coefficient**, L_c.

$$L_c\ (\%) = \frac{A_L\ (Bq \cdot l^{-1})}{A_s (Bq \cdot g^{-1})} \cdot \frac{V_t\ (l)}{P_{1i}\ (g)} \cdot 100$$

LEACHING TEST

Table 5. Water absorption coefficients, ^{238}U and ^{210}Po concentrations, and leaching coefficients with respect to pH

Sample	pH	Ac (wt%)	^{238}U (mBq L^{-1})	^{210}Po (mBq L^{-1})	^{238}U Lc (%)	^{210}Po Lc (%)
Reference SPC-21	**2**	**1.63**	**80 ± 3**	**<0.01**	**0.27**	**<0.01**
	4	**1.01**	**143 ± 12**	**39 ± 19**	**0.48**	**0.19**
	6	**1.25**	**78 ± 5**	**17 ± 11**	**0.26**	**0.09**
	8	**0.95**	**10.6 ± 0.3**	**< 1**	**0.03**	**<0.01**
	10	**0.75**	**< 1**	**< 1**	**<0.01**	**<0.01**
SPC- PG 21-30	**2**	**1.50**	**1090 ± 50**	**970 ± 70**	**1.17**	**0.18**
	4	**1.86**	**730 ± 50**	**150 ± 30**	**0.78**	**0.03**
	6	**1.99**	**1140 ± 40**	**67 ± 17**	**1.22**	**0.01**
	8	**1.46**	**90 ± 30**	**< 10**	**0.09**	**<0.01**
	10	**0.87**	**50 ± 10**	**< 10**	**0.05**	**<0.01**
SPC-MD 21-20	**2**	**0.37**	**463 ± 25**	**871 ± 20**	**0.26**	**0.86**
	4	**0.36**	**363 ± 78**	**891 ± 27**	**0.30**	**0.88**
	6	**0.34**	**340 ± 20**	**862 ± 20**	**0.20**	**0.84**
	8	**0.38**	**111± 8**	**906 ± 23**	**0.18**	**0.90**
	10	**0.46**	**9 ± 4**	**807 ± 26**	**0.05**	**0.77**

CONCLUSIONS

- **Detailed information on the composition wastes generated in both titanium dioxide pigment and phosphoric acid industries have been obtained.**
- **The research performed to analyses the possible use of PG and MUD in different waste dosage (10-30 wt%) showed good compressive strengths (55 to 62 MPa to SPC-PG and 36 to 64 MPa to SPC-MD).**
- **Attending to the Activity Concentration Index (I), PG-SPCs can be used without radiological restriction in the manufacture of building materials, while SPC-MDs can be used with radiological restrictions.**
- **Leaching tests for SPC-PG 21-30 and SPC-MD 21-20 showed that leaching coefficients in acidic media are always higher than in alkaline solution. Finally, we can affirm that the potential pollution of waters affected by these cements can be considered negligible, but there is not regulation about this subject.**

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Thank you for your attention

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